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16. ABSTRACT

An accurate estimate of the environmental concentration of a chemical substance resulting from its manufacture, use, and disposal is essential to any organized hazard assessment program. This estimate of dose can then be used in combination with results from laboratory-derived toxicity tests to assess the associated risks to aquatic species. In following this approach, one must consider what the environment does to the pollutant rather than the reverse. Chemical transformations of a pollutant can take many routes, several of the more significant being ionization as typified by simple acid-base equilibria, hydrolysis, photolysis, microbial degradation, volatilization, and partitioning (sorption). In general, first-order equations can be used to estimate each of these reaction rates using expressions that involve a term for the aqueous concentration and a function of some property of the environment such as pH, turbulence, or microbial population size. These major processes are identifiable, experimentally manageable, and can be arranged easily into differential equations expressing the net rate of change under given conditions. By specifying realistic ranges of these environmental properties, an analysis of pollutant changes can be carried out for a wide variety of aquatic environments.

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JOURNAL ARTICLE

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Prediction of Environmental Pollutant Concentration

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ABSTRACT: An accurate estimate of the environmental concentration of a chemical substance resulting from its manufacture, use, and disposal is essential to any organized hazard assessment program. This estimate of dose can then be used in combination with results from laboratory-derived toxicity tests to assess the associated risks to aquatic species. In following this approach, one must consider what the environment does to the pollutant rather than the reverse. Chemical transformations of a pollutant can take many routes, several of the more significant being ionization as typified by simple acid-base equilibria, hydrolysis, photolysis, microbial degradation, volatilization, and partitioning (sorption). In general, first-order equations can be used to estimate each of these reaction rates using expressions that involve a term for the aqueous concentration and a function of some property of the environment such as pH, turbulence, or microbial population size. These major processes are identifiable, experimentally manageable, and can be arranged easily into differential equations expressing the net rate of change under given conditions. By specifying realistic ranges of these environmental properties, an analysis of pollutant changes can be carried out for a wide variety of aquatic environments. Such evaluative models of environmental processes as they affect pollutant behavior have been used to model successfully the aqueous concentration and fate of several pesticide formulations. This approach is useful since it incorporates the dynamics of no real environment but is based on the properties of stylized environments for which we can mathematically specify rather than measure inputs. This modeling approach can ultimately be improved as better understanding of its underlying concepts develops and as our knowledge of environmental processes improves.

KEY WORDS: water pollution, tests, water quality, chemistry, ionization, hydrolysis, photolysis, microbial degradation, separation, sorption, evaluative models, pesticides

Increasingly, emphasis is being placed on assessing hazards associated with pollutants in the environment. Because hazard assessment requires an estimate of the environmental concentration that represents the dose an organism will receive, much current research is directed toward methods

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for predicting exposure. In simplest terms, these methods must rely on predicting the fate of a pollutant, that is, the time varying concentrations existing within ecosystem compartments of interest.

In following this predictive approach, we must emphasize what the environment does to the pollutant rather than the reverse. Moreover, it is implicit that the importance of an environmental pathway is not determined by its demonstrated existence, but rather by its significance in determining the net rate of loss or formation of a pollutant. For example, we may reasonably assume that microbial metabolism of organics can be an important transformation mechanism in water; whether it will in fact result in significant pollutant loss is the important question.

The complexity of ecosystems makes prediction of environmental fate a sobering task, a task often viewed as hopelessly difficult. Until recently, the necessity for such prediction has been largely ignored because pollutants of environmental interest have been widely dispersed; thus, decisions could be based on voluminous field data and studies carried out on the compounds. We are now moving, however, into an era in which, for both legal and pragmatic reasons, more and more decisions must be based on less than comprehensive data. Increasingly, these data will be from the laboratory rather than the field.

A realistic analysis of our ability to predict environmental concentrations of pollutants requires an answer to several questions: What is the purpose of the predictions? What environments do we want to consider? What precision is required? What are the advantages and disadvantages of the chosen approach?

Given that the purpose of the prediction is to aid in environmental decision-making and not to meet strict scientific needs, pollutant concentrations often can be predicted adequately. For a specific pollutant, decision makers may disagree about whether precision is high enough to base a particular decision on the results, but, until the degree of accuracy required is specified, such questions are rhetorical.

The concepts inherent to the process of predicting environmental concentrations should also be considered. For example, while the process of prediction is technical in nature, it is also utilitarian, and to apply "scientific" rather than pragmatic standards for acceptability is both unreasonable and inimical to progress. This is not to say that science does not play an essential role, but rather to insist that the role of science—in this case, environmental science—is to provide the theory for development of a rationale for extrapolation, namely, prediction.

One of the key difficulties in predicting pollutant fate has been the absence of what might be called a theoretical basis for environmental science. In other words, we have been missing an understanding of quantitative, general relationships that describe how physical and chemical properties of pollutants are coupled with properties of the environment to deter-

mine environmental pathways. This paper deals with some emerging concepts that help provide the missing theoretical basis and also with the application of general scientific principles to the development of a quantitative approach for exposure estimation in aquatic systems.

Because general knowledge of environmental processes and methods for predicting their rates is often inadequate, our approach to exposure prediction is presented in terms of the transport and transformation of organics in water. As knowledge of environmental processes increases, this approach, the principles of which are valid for any compound or medium, can be improved.

Environmental Processes

Chemical transformation as a removal mechanism can take many routes, but we will discuss only ionization, hydrolysis, and photolysis. Each of these processes is very common and an enormous store of data exists in the chemical literature concerning their mechanisms and products. The simplest of these is ionization as typified by simple acid-base equilibria.

The importance of equilibrium relationships for inorganic species such as carbonate is well recognized and needs little comment, but the impact of such reactions on transport and transformation of organics is often overlooked.

The importance of these reactions stems from the fact that the charged form (that is, protonated base or acid anion) is unavailable to participate in processes involving uncharged forms. Thus, attempts to describe environmental processes in terms of the total amount of a pollutant will fail unless equilibria that determine the concentration of the active form are also considered. Examples of this are the effect of pH on volatilization of hydrogen sulfide, the partitioning of pentachlorophenol, or the solubilization and nitrosation of amines.

Although hydrolysis of many kinds of compounds occurs by a variety of mechanisms [*1*],[2] most hydrolytic rates can be described by

$$\begin{aligned} \text{rate} &= -\frac{d[\mathrm{P}]}{dt} \\ &= k_{\text{observed}}[\mathrm{P}] \\ &= (k_{\mathrm{OH}^-}[\mathrm{OH}^-] + k_{\mathrm{H}^+}[\mathrm{H}^+] + k_{\mathrm{H_2O}}[\mathrm{H_2O}])[\mathrm{P}] \end{aligned} \tag{1}$$

where [P], [OH^-], [H^+], [H_2O] are, respectively, concentrations of pollutant, hydroxyl ion, hydrogen ion, and water. Based on Eq 1 and knowledge of hydrolytic reactions, in general, several conclusions can be drawn.

[2] The italic numbers in brackets refer to the list of references appended to this paper.

The rate will usually be a function of pH, a fact that must be taken into account before meaningful kinetic data can be developed. Figure 1 illustrates this pH effect for esters of low, intermediate, and high reactivity. Because natural systems are usually buffered, the rate will, in practice, often be first order for a given system. Effects of ionic strength on general acid-base catalysis are expected to be small in the environment, and temperature effects are simply calculated as illustrated in Fig. 2.

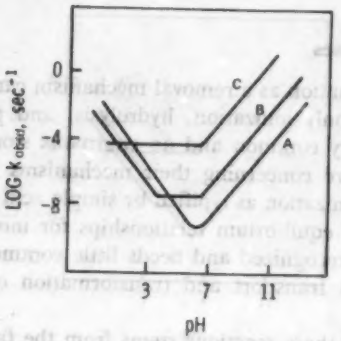

FIG. 1—*Typical pH-rate profile for the hydrolysis of esters: A. less reactive; B. ester of intermediate reactivity; C. highly reactive ester* [2].

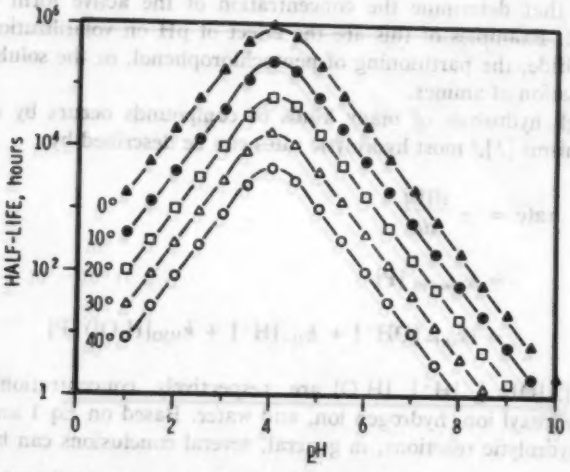

FIG. 2—*Temperature effect on malathion degradation at several pH values* [2].

Photolysis can occur by direct absorption of light, by sensitization via energy transfer, or by indirect processes [2]. In natural waters, the rate of direct photolysis can be readily calculated given the quantum yield, absorption spectrum of both water and compound, latitude, time of day, and time of year [3]. Light intensity is variably attenuated by natural waters, and photochemical rates are strongly depth-dependent in most water bodies. Thus, rapid photolysis in a shallow water sample exposed to light does not necessarily mean that photolysis is an important mechanism in all aquatic environments.

Sensitized reactions and indirect mechanisms are less well understood but similar to direct photolysis in their dependence on light intensity. Current work indicates that direct and sensitized rates are first order, related to the amount of colored matter in water, and that the net rate is the sum of these and the indirect rate. A recent example of a sensitized reaction is given by Zepp [4] who established that singlet oxygen is photochemically generated in a variety of natural waters. In natural water samples, the direct and sensitized processes have been shown to obey a first-order rate law of the form

$$-\frac{d[\mathrm{P}]}{dt} = kI\phi[\mathrm{P}] \tag{2}$$

where I is the incident light intensity and ϕ is the quantum yield. Also, the best current evidence indicates that, under conditions found in aquatic systems, photochemistry is likely to be only slightly affected by such factors as temperature and ionic strength.

Microbial degradation of aquatic pollutants has frequently been suggested as the pathway by which pollutants are most often degraded; however, few kinetic studies, and even fewer system studies, are available to support that conclusion. Most efforts to describe microbial degradation rates of pollutants have used some modification of Monod kinetics [5–8]. Many studies have also shown that nutrient utilization can be described by this expression [9,10], and it has provided a satisfactory basis for numerous studies in the area of biological waste treatment [11]. In spite of these studies, valid questions can be posed concerning: (*a*) the role of anaerobiosis, (*b*) the effect of multiple nutrients, (*c*) the importance of cometabolism, and (*d*) the size of the active microbial population.

In the absence of data to the contrary, however, it seems that the Monod expression (Eq 3) can provide a reasonable first approximation to the rate of microbial degradation in aquatic systems.

$$\text{rate} = -\frac{d[\mathrm{P}]}{dt} = \frac{k[\mathrm{P}][\mathrm{M}]}{k_s + [\mathrm{P}]} \tag{3}$$

where [M] is the concentration of active organisms, and k and k_s are constants. Table 1 shows a comparison of data on bacterial degradation by mixed populations under these conditions. The environmental chamber study was carried out with mixed bacterial populations in a simulated stream system, under conditions in which alkaline chemical hydrolysis of malathion and growth on glucose occurred simultaneously with microbial breakdown of the pesticide. Under these conditions, agreement between the conventional laboratory studies and those in more complex systems is quite reasonable. But, kinetics of microbial degradation, particularly in natural waters by natural populations, is an area that needs much research.

TABLE 1—*Malathion degradation rate coefficients.*

	Alkaline Degradation	
pH	$k_1(M^{-1}s^{-1})$, AEcoS[a]	$k_1(M^{-1}s^{-1})$, Laboratory[b]
7.5	3.86 ± 0.11	5.4 ± 0.1
8.25	4.12 ± 0.47	5.4 ± 0.1

	Microbial Degradation			
	Flask Experiments[c] 0.01 to 0.1 mg/litre	Flask Experiments[d] 0.7 mg/litre	AEcoS[a] 0.5 to 1.0	Chemostat[d] 0.96
$k(10^{-12}$ litre org^{-1} h$^{-1})$	2.6 ± 0.8	2.09 ± 1.9	1.3 ± 0.52	5.46 ± 1.11

[a] From Falco et al [8].
[b] From Wolfe et al [37].
[c] From Paris et al [5].
[d] From Falco et al [38].

Air-water transport has received attention, mostly in the context of transport of gases from air to water [12–14]. Work by Woodwell et al [15], however, established the potential importance of air transport of DDT and led to other studies of this process. In particular, the work of Liss and Slater [12] and Mackay and Leionen [16] have provided a basis for examining the importance of volatilization. Recently, Dilling [17] found good agreement between measured half-lives for about 20 industrial chemicals and half-lives calculated by the method of Mackay and Leionen [16]. Dilling's method is based on an assumption of complete mixing and mass transfer across boundary layers. Under these conditions, the rate of loss from a completely mixed water layer of depth, L, is given by

$$\text{rate} = -\frac{d[P]}{dt} = \frac{k_{il}([P] - P_i/H_i)}{L} \tag{4}$$

where H_i and P_i are the Henry's law constant and partial pressure of pollutant, respectively, and k_{iL} is the mass transfer coefficient.

An alternative approach has been based on a variation of the method used by Tsivoglou [*13*] for measurement of stream reaeration. This method takes advantage of the fact that, although the rate constant for air-water exchange is a function of turbulence, the ratio of rate constants for exchange of two different materials is independent of turbulence. Thus, the rate of volatilization can be expressed as

$$\text{rate} = -\frac{d[P]}{dt} = -k_2\left(\frac{k_p}{k_2}\right)[P] \qquad (5)$$

where k_2 and k_p are the rate constants for reaeration and volatilization, respectively, and [P] is the pollutant concentration. Three attractive features of this approach are: (*a*) the ratio k_p/k_2 is easily measured in the laboratory; (*b*) the reaeration rate coefficient k_2, not in parentheses, is a commonly measured field parameter; and (*c*) the value of k_p/k_2 can be estimated sometimes from first principles if assumptions of spherical molecular symmetry and the absence of solvent interaction are justified. This latter approach has been applied to elemental mercury on a computational basis [*18*] and to vinyl chloride after measurement of the ratio in the laboratory [*19*].

Table 2 gives a comparison of experimental and calculated data for several compounds. Although the calculated values of benzothiophene and methyl parathion are not shown, their molecular diameters are similar to those of the chlorinated biphenyl and they might be expected to have similar values of k_p/k_2. The data for methyl parathion, however, illustrate that strong interaction with water can be expected to invalidate this computational approach by several orders of magnitude.

TABLE 2—*Volatilization rate constants.*

Compound	k_p/k_{O_2} Measured	k_p/k_{O_2} Calculated
Aroclor 1242	0.22 ± 0.04[a]	
Aroclor 1016	0.25 ± 0.04[a]	0.26[b]
Vinyl chloride	2.3 ± 0.3[d]	0.83 to 0.87
Benzothiophene[c]	0.29 ± 0.16	...
Methyl parathion[c]	$\approx 10^5$	...

[a] Average and standard deviation of at least six separate determinations at each of three different turbulence levels.

[b] Calculated based on the longest dimension of 4,4'-dichloro-biphenyl as measured on Dryden models.

[c] Smith, James, Stanford Research Institute, Menlo Park, Calif., personal communication.

[d] From Hill et al [*19*].

Sorption (partitioning) of compounds between water and biotic and abiotic solids occurs in all aquatic systems and is perhaps the single most important environmental process affecting pollutant fate. Sorption from water occurs by several important mechanisms depending on the nature of sorbate and sorbent. For ions or highly insoluble organics, ion exchange and hydrophobic bonding are probably most important and can be described by an equilibrium expression. At the very low concentrations found in the environment, isotherms of the simple form shown in Eq 6 are sufficient to describe this process

$$K_p = \frac{[P]_A}{[P]} \tag{6}$$

where $[P]_A$ and $[P]$ are equilibrium concentrations of pollutant in sorbent and water, respectively. Sorption of both organics and inorganics by sediment and biota has been extensively studied and, in general, five observations can be made regarding this process.

1. Sorption of highly insoluble organics by sediments and microorganisms is rapid (that is, substantially complete in less than a few hours) [*6,20*].
2. Sorption of highly insoluble organics by sediments and microorganisms is rapidly reversible.
3. Sediment sorption is strongest (K_p is greater) with the finer particle size fractions in the case of both cation and hydrophobic organics. (Table 3 shows the effect of particle size on sorption by both hydrophobic (methoxychlor and pyrene) and cation exchange (paraquat) mechanisms.)
4. Unless cation exchange is involved, the most insoluble compounds are usually the most strongly sorbed or most highly accumulated, that is, they have the largest K_ps.
5. Organic cations are likely to be strongly sorbed. Studies with pesticides by Paris et al [*6*] and polycyclic aromatic hydrocarbons by Herbes

TABLE 3—*Particle size dependence of partition coefficient.*

Size Fraction	K_{oc}[b]		K_p
	Methoxychlor	Pyrene	Paraquat[a]
Sand	22 000 (0.73[c])	19 000 (0.53)	400
Coarse silt	73 000 (0.22)	92 000 (0.20)	25 000
Medium silt	88 000 (0.16)	128 000 (0.04)	35 000
Fine silt	93 000 (0.16)	122 000 (0.15)	250 000
Clay	81 000 (0.15)	109 000 (0.11)	750 000

[a] From Karickhoff and Brown [*27*].
[b] $K_{oc} = K_p$/fraction organic carbon.
[c] Coefficient of variation of K_{oc} in three to five sediments from different locations.

[20] are typical of many that have demonstrated this behavior with microorganisms.

The data for methoxychlor and pyrene illustrate an important point usually overlooked in environmental studies, namely, that the extent of accumulation or sorption is not always determined by water solubility. Thus, we find, contrary to usual expectations, that methoxychlor, the most insoluble, is also the least strongly sorbed. In fact, both solubility and hydrophobicity are related to the real driving force for sorption—fugacity or "escaping tendency from water." Such correlations, if they are to hold for compounds of similar solubility, should be related to a property like the octanol-water partition coefficient or vapor pressure that reflects the escaping tendency of the solute.

A factor further affecting our ability to use partition coefficients for sediments and microorganisms is their constancy from location to location or from one organism to another.

In the case of microorganisms, many studies have shown agreement within a factor of 2 to 3 between different organisms [21] and suspended matter [22] in water. It is also probable that some of the environmental changes in complex mixtures such as toxaphene are the result of selective sorption of components [23].

For soils, considerable data indicate that variation from site to site can be expected to be within a factor of 2 to 3. For example, a study by Talbert and Fletchall [24] of 5 triazines on 25 soil types reports coefficients of variation ranging from 40 to 54 percent for 3 of the compounds and of 99 and 145 percent for the other 2. Site to site variation in the K_ps is likely to be acceptable for many purposes even if uncorrelated measurements on whole sediments are used as shown in Table 4 for polychlorinated biphenyls (PCBs). The result of adjustment for the effect of organic content [25, 26] and particle size distribution [27] should further reduce variability of such data. For example, the methoxychlor and pyrene data in Table 3 are for several sediments from different sources and the variability after correction for organic content (K_{oc}) is much less than might be expected.

Another significant effect of partitioning is its impact on the dissolved pollutant concentration, P, and the resulting rate effect on environmental processes. The partition coefficient can be rewritten as

$$K_p = \frac{[P]_s/[S]}{[P]} = \frac{[P]_s}{[S][P]} \tag{7}$$

where $[P]_s$ is the mass of sorbed pollutant per unit solution volume and [S] is the mass of sorbent per unit solution volume, that is, the ratio of sediment to water. Mass balance of P gives

$$[P]_T = [P]_s + [P] \tag{8}$$

TABLE 4—*Partition coefficients for chlorinated biphenyls on sediments from different sites.*

Sediment	Partition Coefficient × 10^{-3}	
	2,5,3′,4′	2,6,2′,6′
Hickory Hill Pond	1.18 ± 0.11	1.27 ± 0.22
Doe Run Pond	0.99 ± 0.08	1.08 ± 0.13
U.S. Department of Agriculture Pond	0.58 ± 0.06	0.65 ± 0.04
Oconee River	0.42 ± 0.09	0.51 ± 0.07

where $[P]_T$ is the total mass of pollutant in a unit volume of liquid containing S grams of sorbent. Substitution of Eq 8 in Eq 7 gives Eq 9 for the fraction of total pollutant dissolved

$$\frac{[P]}{[P]_T} = \frac{1}{[S]K_p + 1} \tag{9}$$

Figure 3 shows how the fraction in solution varies with [S] for different values of the partition coefficient. It is easily seen that unless sediment to water ratios are high or partition coefficients large, much of the pollutant will be in the solution phase. This finding is consistent with recent data by Miles [*28*] who found that even DDT and DDE in several Canadian streams were 10 to 80 percent in the solution, that is, unadsorbed. Thus, even though the concentration of a pollutant may be much higher in sediment than in the water column, a significant fraction of the total *amount*, in many cases, may be in the water.

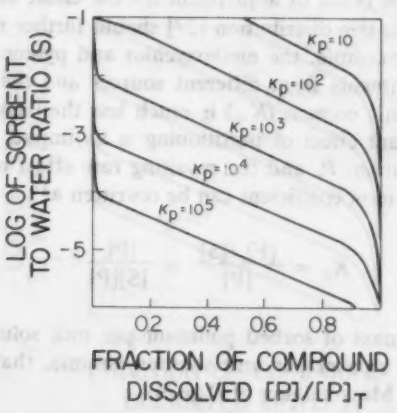

FIG. 3—*Plot of fraction of total compound dissolved versus ratio of sorbent to water for given values of partition coefficients* [39].

The net effect of sorption is to "buffer" the concentration and reduce the rate of change in the amount of pollutant in the system. This is readily demonstrated as follows.

In all of the foregoing, rates were shown to be described by equations in the form

$$-\frac{d[P]}{dt} = k[P] \tag{10}$$

or the equivalent second-order rate expression. In this equation, [P] is the "true" solution concentration, which in the case of a simple laboratory experiment is also the total amount of pollutant per unit volume of liquid. It can readily be shown that for any rate process that is slow compared to sorption-desorption

$$-\frac{d[P]_T}{dt} = \frac{k}{K_p[S] + 1}[P]_T \tag{11}$$

where $[P]_T$ is the total amount of pollutant divided by the system volume, K_p is the partition coefficient, [S] is the ratio of sediment mass to water volume, and k is the rate constant for the process in the absence of sorption.

This observation leads to the important conclusion that unless transformation occurs nearly as fast or faster in the sorbed form, the net effect of sorption will be to reduce the rate of transformation. The reduction in rate constant over that of the true solution value is given by the factor $1/(k_p[S] + 1)$. It is perhaps worth noting that this application of a rapid prior equilibrium has been widely used in mechanistic chemistry and even describes chemical reaction in the presence of solvent partitioning [*29*].

Applications of this principle are best illustrated by two examples. The first, Fig. 4, shows the expected effect of sorption on the half-lives of DDT and methoxychlor at pH 8 for which, in the absence of sorption, the rate constants are equal. Figure 5 shows Hamelink and Waybrant's data [*30*] for loss of DDE from a quarry compared with a prediction based on use of their partition coefficient to adjust rate constants for photolysis and volatilization. In addition to these examples, studies in our laboratory have shown that partitioning of PCBs influences volatilization of these compounds according to prediction [*31*].

If we assume that the foregoing relationships can adequately predict the rates and extent of environmental processes and that the generalizations are reasonable, then several important conclusions can be drawn.

1. All of the rate processes can be estimated by expressions that involve a term for the aqueous concentration [P].
2. Each rate is a function of properties of the aquatic environment such as pH, turbulence, or microbial population size.

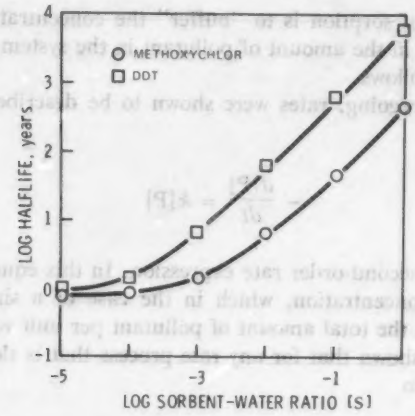

FIG. 4—*Plot of methoxychlor and DDT hydrolysis half-lives versus sorbent-water ratios at pH 8.*

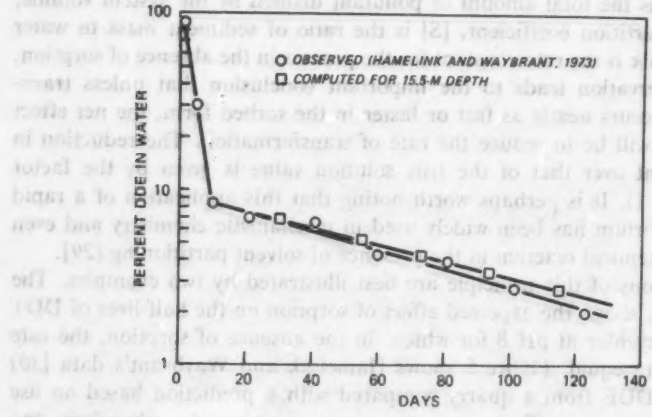

FIG. 5—*Loss of DDE from the water column of an Indiana quarry.*

3. Although half-life can be a useful parameter for comparing rates under similar conditions, it has little value for prediction of lifetime even for laboratory studies unless concentration dependence is described. More importantly, half-life has no meaning either without context to a mathematical relationship or for a system to which there is a continuous input as in most natural environments. Under these conditions, the steady state or time-varying concentration based on input and output is the exposure level that an aquatic organism encounters.

Assessment Method—Evaluative Models

Given the preceding, the decision maker is still left with the problem of deciding how to estimate exposure and in what system. Ideally (from a practical viewpoint), it is desirable that the estimation procedure be objective, quantitative, and systematic, and that it provide a rationale for extrapolation. Because objectivity can never be fully attained, subjective views should be made explicit in the statement of the assumptions. There is no feasible way to attain this without recourse to a mathematical framework because the problem is both computational and complex. The framework synthesizes our knowledge or hypotheses of pollutant properties, environmental processes, environmental characteristics, and their interrelationships into an explicitly stated mathematical "model." The complexity necessitates the use of computer techniques in most cases.

The major processes are identifiable and experimentally manageable, and can be easily arranged into differential equations expressing the net rate of change except for the problem of specifying conditions. Because each term contains a reference to the environment, for example, pH, light intensity, temperature, etc., it is clear that any computation requires the specification of an environment. Furthermore, the sources and physical terms (washout, flow-through) must be specified if the computations are to be meaningful. If models are to be site-specific, these requirements represent unrealistic and frequently impossible tasks because too many field measurements on the chosen sites would be required. Moreover, the number of potential sites of interest is almost infinite and the number of chemicals very large, so a procedure is needed that will permit generalization about properties both of environments and of pollutants in terms consistent with the relatively small number of transport and transformation pathways.

Because the properties of the environment that are relevant to process rates and extent are identified in the individual process terms, there are about as many properties as there are processes. The relationship is not exact, however. For example, the description of light intensity requires that more than one parameter be specified. Some of the processes occur by physical transport mechanisms, and the property to be specified (for example, dispersion) cannot be easily measured.

Rather than *always* requiring site specificity, an alternative approach is to evaluate the influence of the properties of the environment on the fate of the pollutant. This evaluation is accomplished by seeking ranges of the environmental properties within which there is variation in the fate of the pollutant. These "ranges of sensitivity" then can be used to evaluate further whether site specific studies are needed prior to decision-making. This type of analysis can be carried out for a given pollutant and for a wide variety of environments. We have called models for this purpose "evaluative" because they incorporate the dynamics of no specific environment but are based on

the properties of stylized environments or hypothetical pollutants for which we specify (rather than measure) inputs. This presents the possibility of examining the environmental behavior of hypothetical pollutants, or even choosing among several related chemicals for use in a given situation by balancing properties to meet the need while ensuring that the fate is acceptable by some criterion.

Evaluative models in the context discussed here have been slow to evolve although similar approaches have been applied to air problems [*32*]. In water, a simple model was used by Hill et al [*19*] to examine the behavior of vinyl chloride in specified aquatic environments. Lassiter et al [*33,34*] and Lassiter and Malanchuk [*35*] also examined mercury in stylized aquatic systems.

Recent work with several organics involves a simple nine compartment model, which can be used as shown in Fig. 6 to simulate ponds, streams, or lakes.[3] Typical input parameters for the three kinds of systems are shown in Table 5. Environmental processes included in the model are: microbial, hydrolytic, photochemical, and free radical, oxidative, degradation; sediment and microbial sorption; volatilization; and advection. The model itself is a series of differential rate equations consisting of a sum of terms such as those already discussed plus agebraic equations for sorption. Figures 7 and 8 are computer simulations showing the predicted rates of various pathways of methyl parathion loss in a shallow pond and in an oligotrophic lake. Note that in the case of the pond, microbial degradation is dominant, whereas in the deep clear lake, photochemistry is more important. The same rate constants were used in both simulations.

Figure 9 is shown to illustrate the expected importance of volatilization from a river where air-water exchange overrides the other loss mechanisms. It is, of course, a simple task to change the form of display, input rate, simulated time, degree of resolution, etc.

Analysis

Current understanding of relevant parameters affecting the environmental fate of a pollutant leads to the conclusion that evaluative models can be a beneficial aid in exposure assessment. The parameters considered include properties of both the chemicals and the stylized environment. The approach can be improved as better understanding of its underlying concepts develops and as our knowledge of environmental processes improves.

Imprecision of the predictions for real environments based upon use of the model for stylized environments will be seen by many as a disadvantage; however, evaluative models are not intended for prediction of detailed fate in specific environments. Rather, the intent is to generalize for a broad

[3] Lee, S. S. and Holt, B. R., Stanford Research Institute, Menlo Park, Calif.

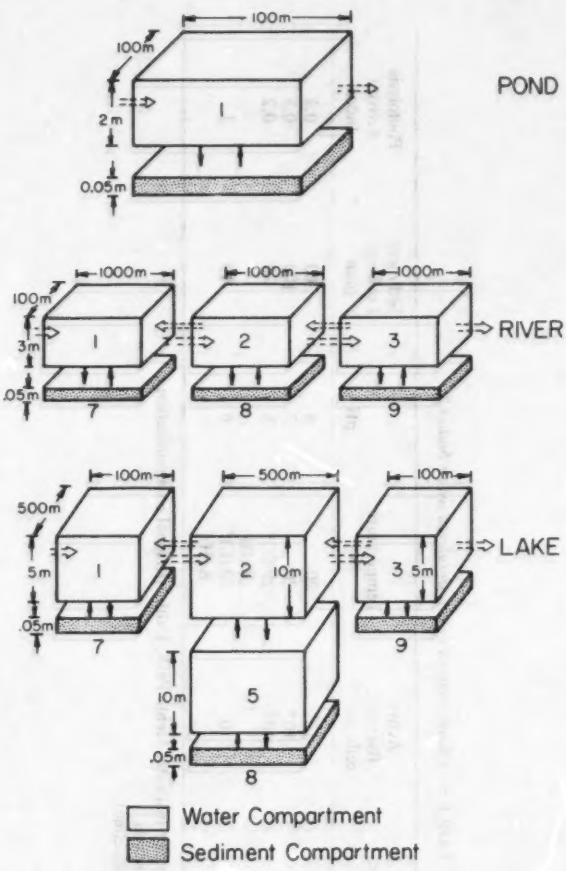

FIG. 6—*Physical configurations of the pond, river, and lake simulations (see footnote 3).*

range of situations, so that the need to make more detailed studies can be evaluated.

Although it is true that no single model can be expected to be sufficient for every possible case, the model should be parameterizable so that one model can handle a wide variety of cases. Furthermore, evaluative models can be designed and constructed to facilitate ease of use by nonspecialists.

Like every other model, an evaluative model is subject to the standard criticism that it should be validated, but models of this complexity cannot be validated in the same sense that a hypothesis is tested. This problem stems from the fact that a model is a collection of hypotheses and, thus, is

TABLE 5—*Characteristics of the simulated water bodies.*[a]

Type of Water Body	Total Bacteria, cells, ml^{-1}	Active Bacteria, cells, ml^{-1}	Temperature, °C	pH	Sediment Loading, ppm	Photolysis Activity Index
Pond	10^6	10^5	20	8	300	0.2
Stream	10^5	10^4	20	7	100	0.5
Eutrophic lake	10^6	10^5	20 (E)[b] 8 (H)[c]	8	50	0.2
Oligotrophic lake	10^2	10	20 (E)[b] 8 (H)[c]	6	10	1

[a] Lee, S. S. and Holt, B. R., Stanford Research Institute, Menlo Park, Calif., personal communication.
[b] (E) = epilmnion (water above the thermocline).
[c] (H) = hypolimnion (water below the thermocline).

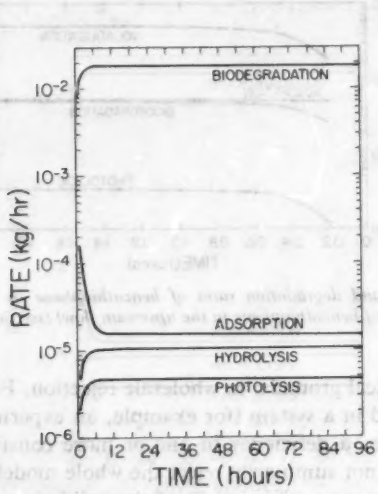

FIG. 7—*Transport and degradation rates of methyl parathion in pond simulation (see footnote 3).*

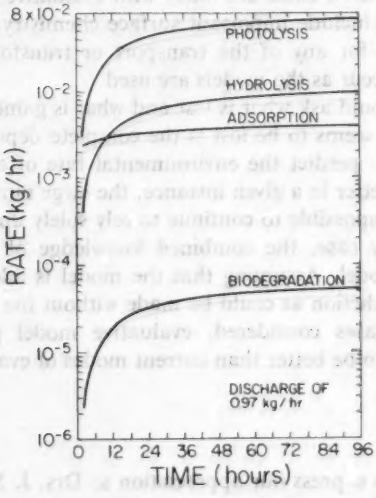

FIG. 8—*Transport and degradation rates of methyl parathion near the discharge into the simulated oligotrophic lake (see footnote 3).*

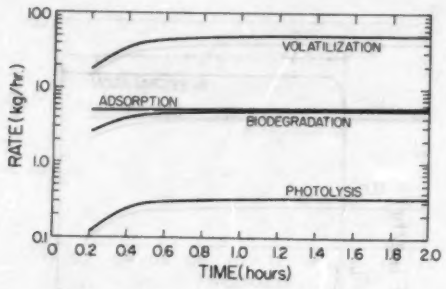

FIG. 9—*Transport and degradation rates of benzothiophene in compartment 1 in the simulated river (1 ppm of benzothiophene in the upstream flow) (see footnote 3).*

not subject, on logical grounds, to wholesale rejection. Failure to reproduce the results observed in a system (for example, an experimental microcosm) can be attributed to a deficiency in one or more constituent parts of the model. One would not summarily reject the whole model, but rather would correct the defective part. This aspect of the validation problem [*36*] illustrates that the nature of system models is much like that of a scientific theory: only piecemeal testing is possible. Seldom is an entire theory rejected. Usually it evolves into a more inclusive theory by rejection and replacement of constituent parts, or it broadens by addition of concepts that had been missing. Both cases are likely with evaluative models. The addition of concepts to include important surface chemistry, or substitution of better descriptions for any of the transport or transformation processes, will undoubtedly occur as the models are used.

Finally, we should ask what is lost and what is gained by using evaluative models. What seems to be lost is the complete dependence upon individual "experts" to predict the environmental fate of a substance. While experts might do better in a given instance, the large number of new chemicals will make it impossible to continue to rely solely upon the expertise of individuals. In any case, the combined knowledge of experts should be reflected by the model. Assuming that the model is adequate, we gain at least as good a prediction as could be made without the model, and potential errors and biases considered, evaluative model predictions should generally turn out to be better than current modes of evaluation.

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